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(54) SELECTIVE BACTERIAL CYCLIC LEACHING PROCESS

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ABSTRACT OF THE DISCLOSURE:

A biohydrometallurgical process for the selective extraction of cadmium, copper and zinc values from lead ores or concentrates containing these metals and lead in the form of their respective sulphides. The process comprises (a) grinding the lead ore or concentrate to form small solid particles; (b) contacting the surfaces of the small solid particles with an aqueous nutrient medium to form a leach suspension, the aqueous nutrient medium having a pH of 1.5 to 4.0, containing sulfuric acid and being maintained at a temperature of 20° to $40^{\circ}C$; (c) inoculating the leach suspension with a strain of adapted aerobic autotrophic iron and sulfur-oxidizing Thiobacillus ferrooxidans; (d) agitating the inoculated leach suspension and simultaneously aerating the suspension with carbon dioxide enriched air, as the leaching of the metals at the surfaces of the particles progresses; and (e) filtering the leach suspension to obtain a liquid fraction from which are recovered the extracted metal values.

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The pr[illegible]t invention is concerned with[illegible]rocess for removing and selectively recovering the cadmium, copper and zinc values from lead ores or concentrates containing these metals and lead in the form of their respective sulphides by means of an iron and sulfur-oxidizing bacteria, such as *Thiobacillus ferrooxidans*.

There is a plurality of processes which involve the use of certain bacteria, such as *Thiobacillus ferrooxidans*, in the hydrometallurgical treatment of metal sulphides; a number of these are described in the following patents: U.S. Patent Nos. 2,829,964; 3,218,252; 3,252,756; 3,260,593; 3,272,621; 3,305,353; 3,347,661; 3,455,679; 3,607,235 and 3,679,397; Canadian Patent No. 744,701 and Belgian Patent No. 794,526.

The most commonly used processes for extracting the cadmium, copper and zinc values from off-grade lead sulphide concentrates, wherein lead, iron, zinc, copper and cadmium tend to occur together, particularly where the mineralization consists of crystalline intergrowths of their respective sulphides, usually present many technical difficulties. As the zinc and cadmium values are normally carried in the slags that result from the lead smelting operations, their recovery from such slags involves a high-acid leaching treatment of the slag or a reduction-fuming of the molten slag.

It is an object of the invention to provide an improved biohydrometallurgical process for the selective extraction of the metals in pure from directly from lead ores or concentrates containing same, thereby eliminating the necessity of further treating the ores or concentrates following the recovery of lead in smelters.

In accordance with the present invention, there is thus provided a biohydrometallurgical process for the selective extraction of cadmium, copper and zinc values from lead ores or concentrates containing these metals and lead in the form of their respective sulphides, which comprises:

a) grinding the lead ore or concentrate to form small solid particles;

b) contacting the surfaces of the small solid particles with an aqueous nutrient medium to form a leach suspension, the aqueous nutrient medium having a pH of 1.5 to 4.0, containing sulfuric acid and being maintained at a temperature of 20° to 40°C;

c) inoculating the leach suspension with a strain of adapted aerobic autotrophic iron and sulfur-oxidizing Thiobacillus ferrooxidans;

d) agitating the inoculated leach suspension and simultaneously aerating the suspension with carbon dioxide enriched air, as the leaching of the metals at the surfaces of the particles progresses; and

e) filtering the leach suspension to obtain a liquid fraction from which are recovered the extracted metal values.

The aqueous medium used in this invention contains small quantities of nutrients, e.g., ammonium sulfate and calcium nitrate. The bacterial activity requires an acid medium, at a pH range of 1.5 to 4.0; the best bacterial performance is obtained when the pH is maintained at a constant value of 2.3.

During the leaching, the inoculated leach suspension is agitated and aerated with air containing carbon dioxide in sufficient amount to provide oxygen for the oxidation of the sulfides and carbon dioxide as a carbon source for the growth of the bacteria. The carbon dioxide content of the carbon dioxide enriched air is advantageously comprised between 0.03 and 10% by volume, and is preferably 0.2% by volume.

The concentration of the small solid particles in the leach suspension may be as high as 30% pulp density, preferably 14% pulp density.

In a preferred embodiment of the invention, the leach

suspension is filtered to obtain, one the one hand, a first liquid fraction from which are recovered the extracted metal values in an amount of up to 60% by weight and, on the other hand, a leach residue. This leach residue is ground and a quantity of the same aqueous nutrient medium is added to the ground leach residue to produce a further leach suspension which is inoculated with the strain of the bacteria <u>Thiobacillus</u> <u>ferrooxidans</u>. The leaching step as outlined in (d) is repeated and the further leach suspension is filtered to obtain, on the one hand, a second liquid fraction from which are recovered further extracted metal values and, on the other, a further leach residue which is retained for recovery of the lead therefrom by smelting.

When the ore or concentrate to be treated contains iron, the leaching operation will be seen to form dissolved iron. In such an instance, the pH of the first and second liquid fractions may be increased to about 3.0 to precipitate the dissolved iron in the form of basic ferric sulfate which is removed by filtration, prior to recovering the extracted metal values.

The cadmium and copper can be recovered by cementation with zinc dust and subsequent filtration. The zinc on the other hand can be recovered by increasing the pH of the first and second liquid fractions to about 8.0 to precipitate zinc in the form basic zinc sulfate which is then removed by filtration.

After recovery of the extracted metal values, the aqueous nutrient medium is advantageously recycled to step (b) after having been readjusted in its nutrients content.

An outstanding feature of the present invention is the partial oxidation of lead sulfide to lead sulfate. The latter requires heat during sintering while the former liberates an excess of heat. The presence of lead sulfate in the feed of lead recovery from sulfides has the advantage of reducing the recycle load used to dissipate heat during the conventional sintering process.

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A preferred embodiment of the process according to the invention will now be described in greater detail, with reference to the accompanying drawings, wherein:

FIGURE 1 is a graphic representation of the effect of pulp density, which is the solid to liquid ratio, on the respective rates of extraction of zinc and copper from a -400 mesh lead sulphide concentrate by means of Thiobacillus ferrooxidans at pH 2.3, temperature 35°C and aeration with armospheric air containing 0.2% carbon dioxide;

FIGURE 2 is a graph representing this effect of pulp density, i.e. solid to liquid ratio, on the respective yields of copper and zinc from a -400 mesh lead sulphide concentrate by means of Thiobacillus ferrooxidans at pH 2.3, temperature 35°C and aeration with atmospheric, containing 0.2% carbon dioxide;

FIGURE 3 is a flow diagram of a process according to the invention, for the leaching and recovery of copper, cadmium and zinc from lead sulphide concentrates.

The results illustrating the effectiveness of the method of the present invention in Figures 1 and 2 were derived from shake flask experiments using 250 ml of Erlenmeyer flasks a gratory shaker apparatus and a total volume of 75 ml of leach solution containing 70 ml of iron free nutrient medium, 5 ml of bacterial suspension as inoculum and solid particles of the lead sulphide concentrate in pulp densities of between 2 and 14%. The lead sulphide concentrate utilized had the following composition:

Table 1

Chemical %		Mineralogical
Pb:	42.9	Galena
S_{total}:	29.6	Zinc Blende
Fe:	16.7	Pyrite
Zn:	7.7	Chalcopyrite
Cu:	2.4	Pyrrhotite
Cd:	0.02	

The highest extraction rates, 104.5 mg/(1 hr) for zinc and 114.2 mg/(1 hr) for copper, were obtained for leach suspensions of 12% or higher pulp densities. A linear relationship was found to exist between the ultimate extraction and the pulp density. 70.7% is the best zinc recovery achieved and it was the maximum zinc extraction obtained at a pulp density of 2%; on the other hand the highest copper recovery is 90.9% and it was obtained at a pulp density of 13.4%. Under sterile conditions (in absence of bacteria) the maximum yields were 8.9% and 4.7% respectively for zinc and for copper. The cadmium recoveries were found to closely follow those of the zinc. During bacterial leaching, the concentrations of lead and iron in solution were found to be less than 0.25 g/1 and 3.0 g/1 respectively: As the leaching progressed some basic ferric sulphate salts, jarosite type, and insoluble lead sulphate deposited on the surface of the unreacted solid substrate and impeded the bacterial activity.. However, regrinding the leach residue to expose new surfaces and subsequent leaching resulted in extractions of as much as 98% of the copper, 96% of the zinc and 100% of the cadmium. Therefore, to obtain a relatively complete extraction of these elements from the lead sulphide concentrate, a two-stage leaching process would be preferable. In the first stage, the concentrate could be leached so as

to provide for an estimated yield of 60%, the residue would then be reground and the leaching could be completed in the second stage. It was discovered that during these experiments, approximately 40% of the lead sulphide originally present in the concentrate had been converted by oxidation to lead sulphate.

For further illustration of the applicability of the method of this invention to the extraction of cadmium, copper and zinc, larger scale stirred tank experiments were carried out on 8 and 12 liters batches of leach suspensions of 6 and 14% pulp density respectively, using a -325 mesh size quantity of the lead sulphide concentrate at pH 2.3, temperature 35°C and air enriched to 0.2% in carbon dioxide. The tabulated results thereof are give in the following Table 2.

Table 2

Volume (liter)	Pulp density	Metal Extractions				
		Rate (mg/(1 hr)		Yield %		
		Zb	Cu	Zn	Cu	Cd
8	6	69.2	67.3	66.3	82.4	100
8	14	72.6	64.5	62.1	78.5	100
12	6	70.3	74.6	61.4	81.2	100
12	14	71.2	73.9	59.9	79.3	100

The results of the tank leaching experiments are slightly below those of the shake flask experiments. The discrepancy is attributable to the size differences between the concentrate particles used for the shake flasks experiments, i.e. -400 mesh, and, those used for the tank leaching experiments, i.e. -325 mesh.

After filtration, the leach liquor was found to typically contain 3.5 to 9.0 g/l of zinc, 0.5 to 3.0 g/l of copper, 0.05 to 0.2 g/l of cadmium and 1.2 to 3.0 g/l of ferric iron, depending mostly on the initial pulp density of the leach supsen-

sion. In practice, the leach liquor would preferably be recycled to further increase the metal concentrations.

The flowsheet of figure 3 schematically, outlines of a process for the recovery of minor metal values from lead sulphide ores and concentrates containing said metal values in accordance with the present invention. According to this scheme, it is preferable to remove the ferric iron by neutralisation and precipitation prior to proceeding to the recovery of the other metals. Copper and cadmium were jointly recovered from the iron free liquor by cementation with zinc dust. The pH of the liquor, depleted of the metals which are more noble than zinc, was increased to 7.5 to 8.0 to form a basic zinc sulphate precipitate which was filtered off and from which, after its dissolution in sulphuric acid, it has been possible to recover the zinc by electrolysis. In order to increase the pH of the solution and thus cause precipitation of the basic zinc sulphate, magnesium oxide or lime may be added.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. A biohydrometallurgical process for the selective extraction of cadmium, copper and zinc values from lead ores or concentrates containing said metals and lead in the form of their respective sulphides, which comprises:

a) grinding said lead ore or concentrate to form small solid particles;

b) contacting the surfaces of said small solid particles with an aqueous nutrient medium to form a leach suspension, said aqueous nutrient medium having a pH of 1.5 to 4.0, containing sulfuric acid and being maintained at a temperature of 20^{o} to $40^{o}C$;

c) inoculating the leach suspension with a strain of adapted aerobic autotrophic iron and sulfur-oxidizing Thiobacillus ferrooxidans;

d) agitating the inoculated leach suspension and simultaneously aerating the suspension with carbon dioxide enriched air, as the leaching of the metals at the surfaces of the particles progresses; and

e) filtering the leach suspension to obtain a liquid fraction from which are recovered the extracted metal values.

2. A process according to claim 1, wherein said pH is kept constant at 2.3.

3. A process according to claim 1, wherein said temperature is kept constant at $35^{o}C$.

4. A process according to claim 1, wherein the carbon dioxide content of the carbon dioxide enriched air is comprised between 0.03 and 10% by volume.

5. A process according to claim 4, wherein said carbon dioxide content is 0.2% by volume.

6. A process according to claim 1, wherein the concentration of small solid particles in said leach suspension is of up to 30% pulp density.

7. A process according to claim 6, wherein the pulp density of the leach suspension is 14%.

8. A process according to claim 1, wherein the leach suspension is filtered to obtain, one the one hand, a first liquid fraction from which are recovered the extracted metal values in an amount of up to 60% by weight and, on the other hand, a leach residue; said leach residue is ground and a quantity of the same aqueous nutrient medium is added to the ground leach residue to produce a further leach suspension which is inoculed with said strain of the bacteria Thiobacillus ferrooxidans; the leaching step as outlined in (d) is repeated and the further leach suspension is filtered to obtain, on the one hand, a second liquid fraction from which are recovered further extracted metal values and, on the other, a further leach residue which is retained for recovery of the lead therefrom by smelting.

9. A process according to claim 8, wherein the pH of said first and second liquid fractions is increased to about 3.0 to precipitate dissolved iron in the form of basic ferric sulphate which is removed by filtration, prior to recovering the extracted metal values.

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10. A process according to claim 9, wherein cadmium and copper are recovered by cementation with zinc dust and subsequent filtration.

11. A process according to claim 10, wherein the pH of said first and second liquid fractions is increased to about 8.0 to precipitate zinc in the form of basic zinc sulphate which is removed by filtration.

12. A process according to claim 1, wherein after recovery of the extracted metal values the aqueous nutrient medium is recycled to step b), after having been readjusted in its nutrients content.

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Fig.1

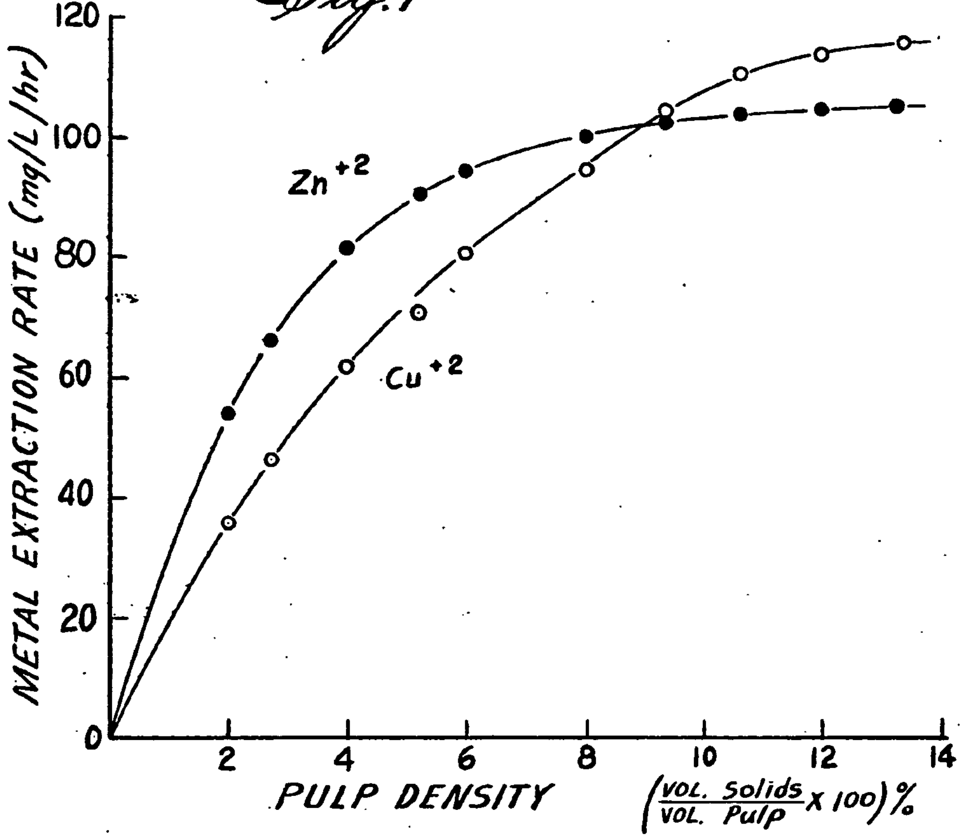
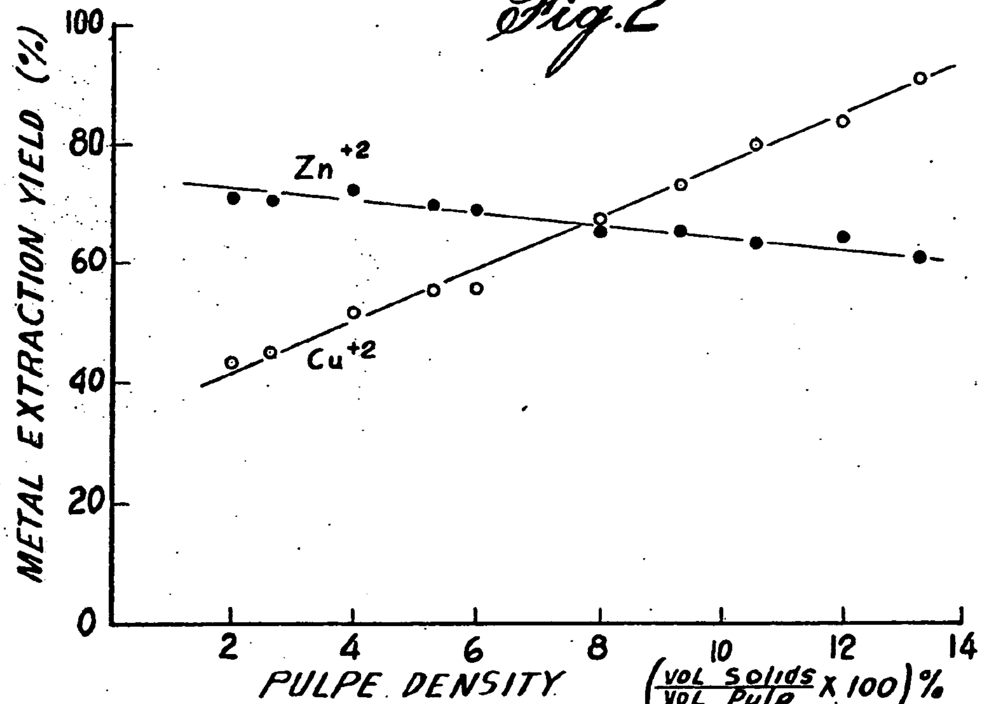


Fig.2



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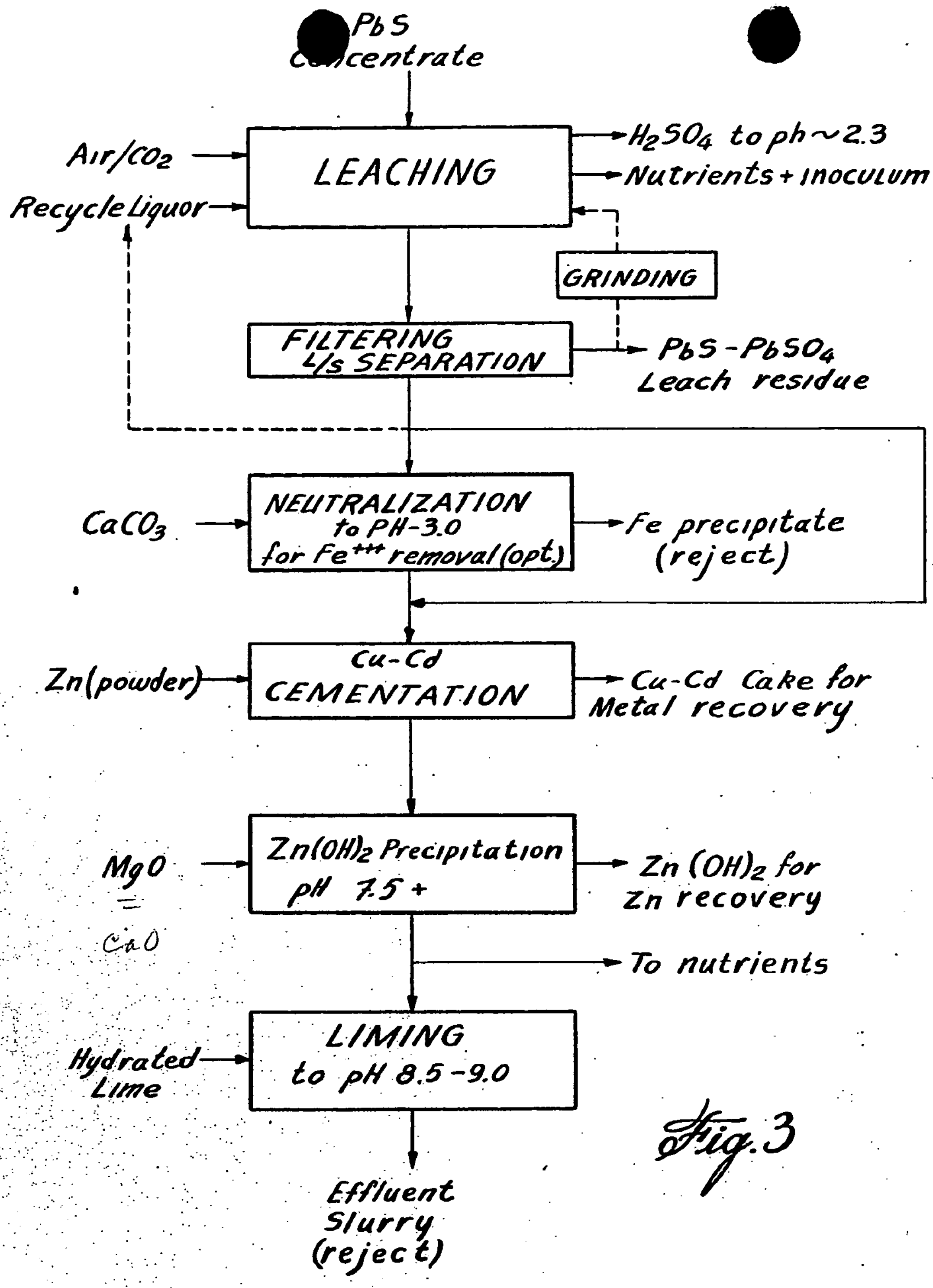

Fig. 3

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